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(71) Applicant
Redland Roof Tiles Limited

(Incorporated in United Kingdom)

Redland House, Reigate, Surrey RH2 0SJ

(72) Inventors
Alan Maries
Colin Douglas Hills

(74) Agent and/or Address for Service
Boult, Wade & Tennant,
27 Furnival Street, London EC4A 1PQ

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C1H 120 620 711 718 796 812 813
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None

(58) Field of search
C1H
B5A
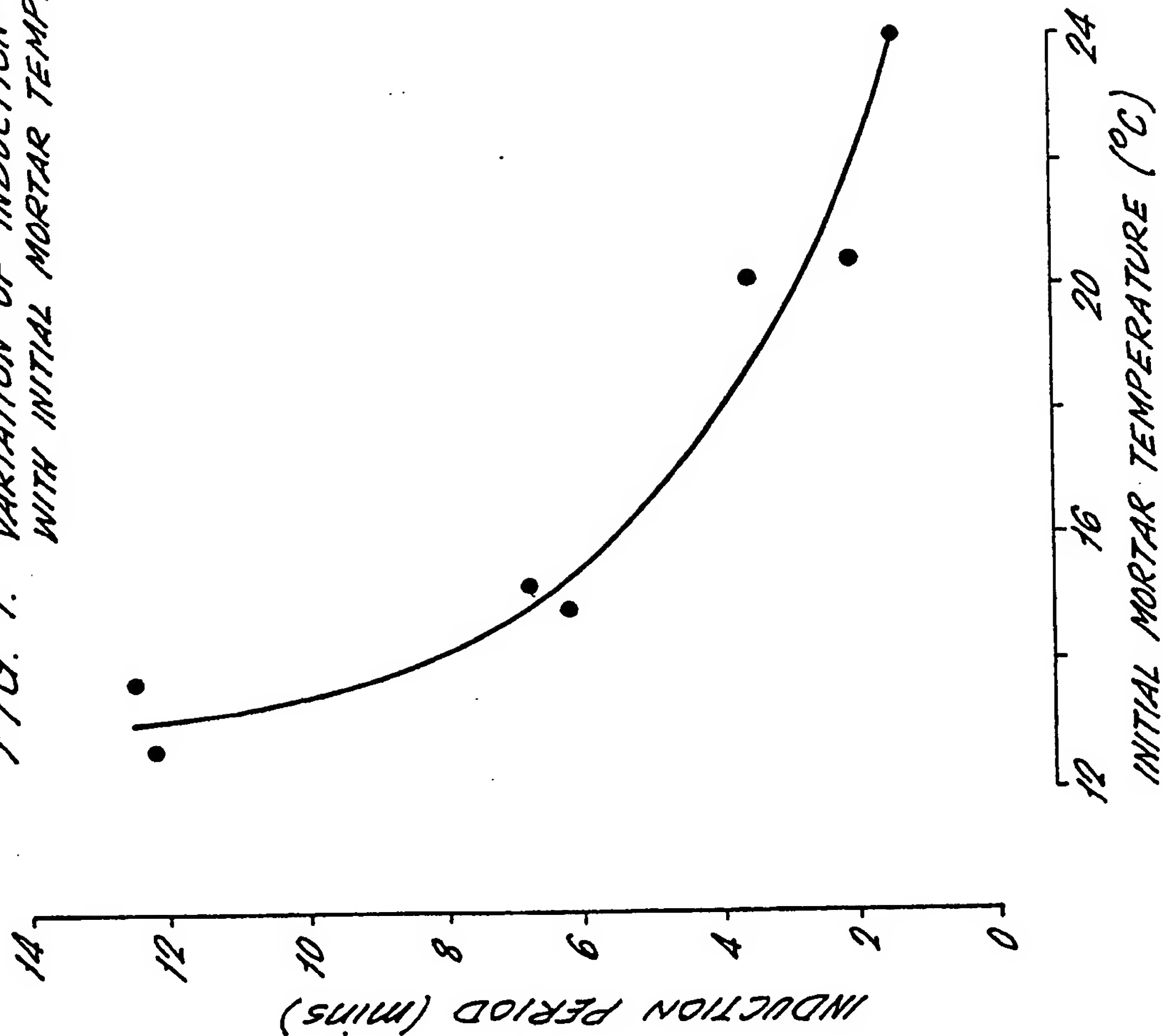**Selected US specifications from IPC sub-class C04B**

(54) **Improvement in concrete articles**

(57) A method of manufacturing concrete articles such as roof tiles wherein the void content of the fresh mortar is from 14 to 23% by volume also comprises the use of carbon dioxide or a carbon dioxide containing medium to accelerate the curing of the mortar.

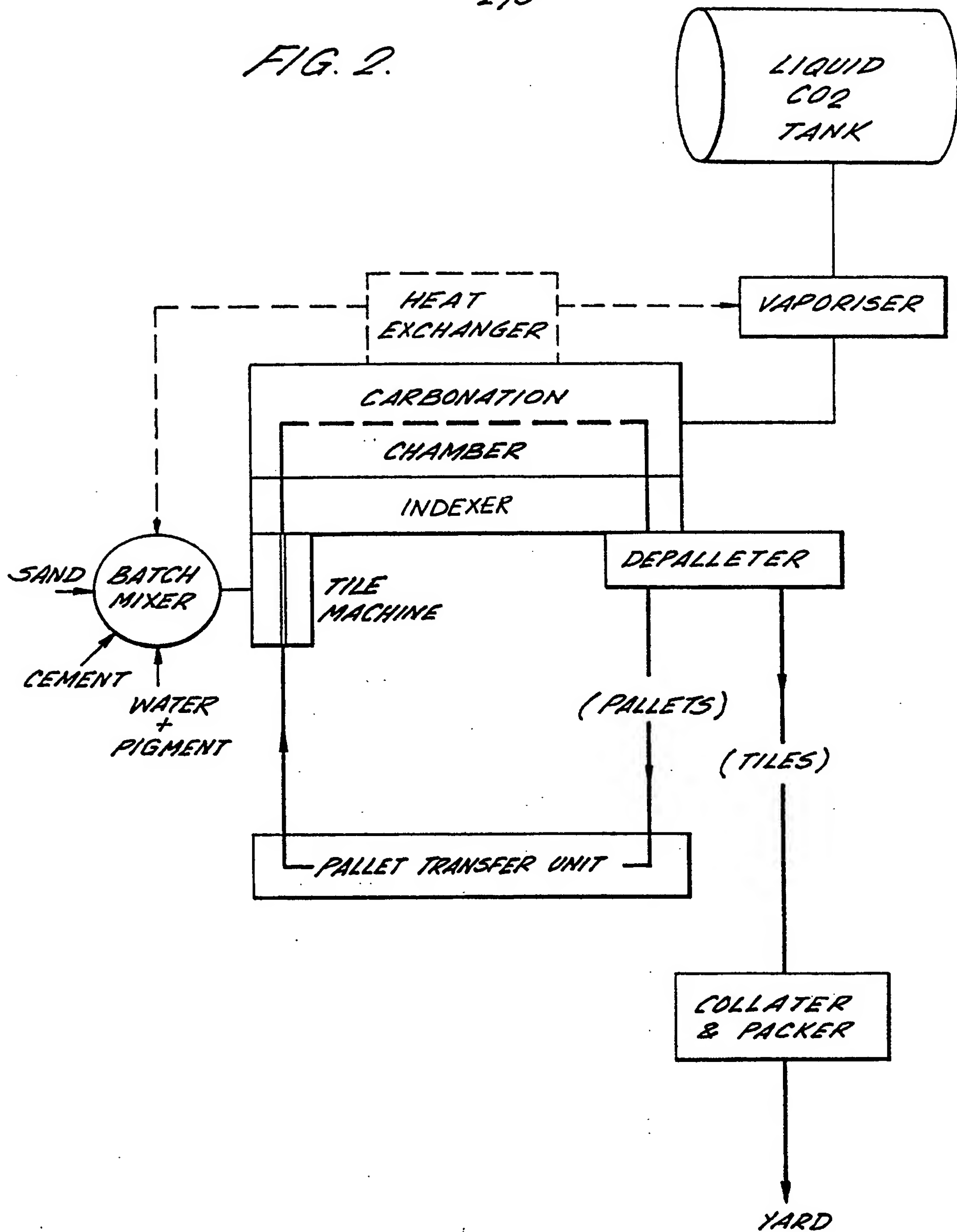Also provided is an apparatus for carrying out this method (Figs. 2, 3 not shown).

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The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

FIG. 1. VARIATION OF INDUCTION PERIOD WITH INITIAL MORTAR TEMPERATURE.

INDUCTION PERIOD (mins)

INITIAL MORTAR TEMPERATURE (°C)

FIG. 2.

FIG. 3.
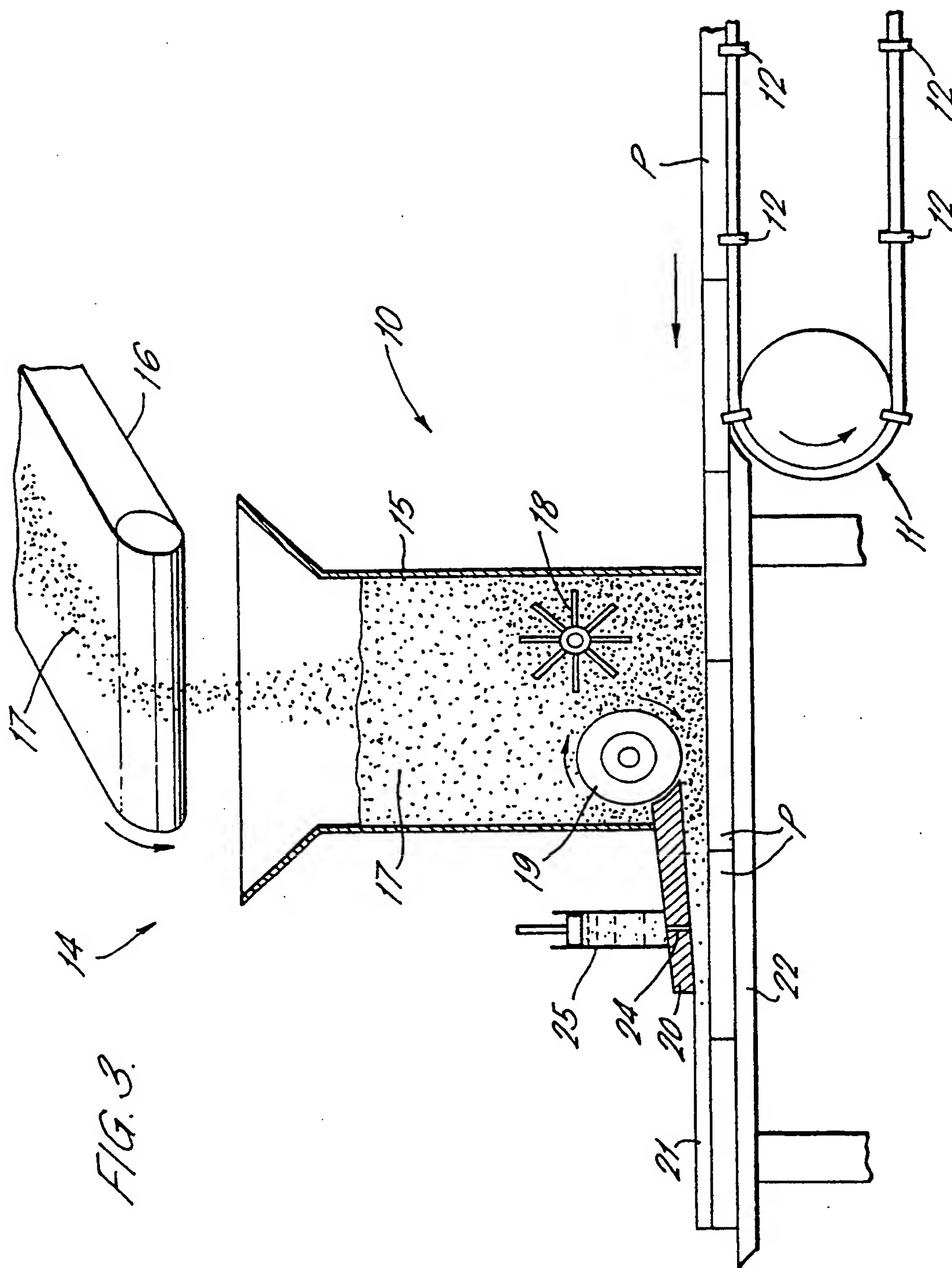
FIG.4. EFFECT OF W/C RATIO ON APPARENT STRENGTH AFTER 15 MINUTES CARBONATION.

● PLAIN
○ + BV40
□ + CEMAIRIN
× + PIGMENT

APPARENT 15-MINUTE STRENGTH (M.PA.)

W/C RATIO

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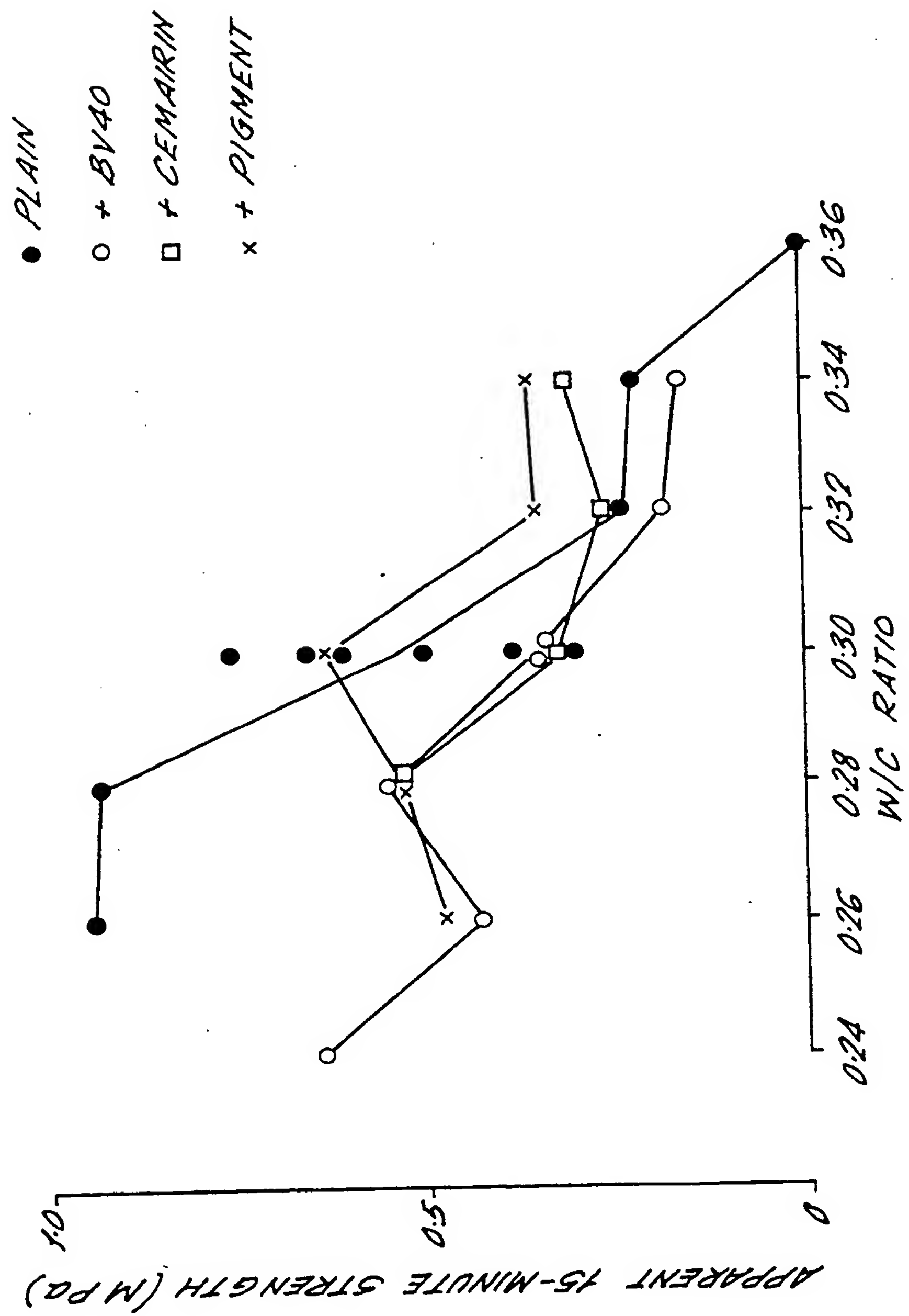
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FIG. 5. BREAKING LOADS AT 4-WEEKS vs W/C RATIO
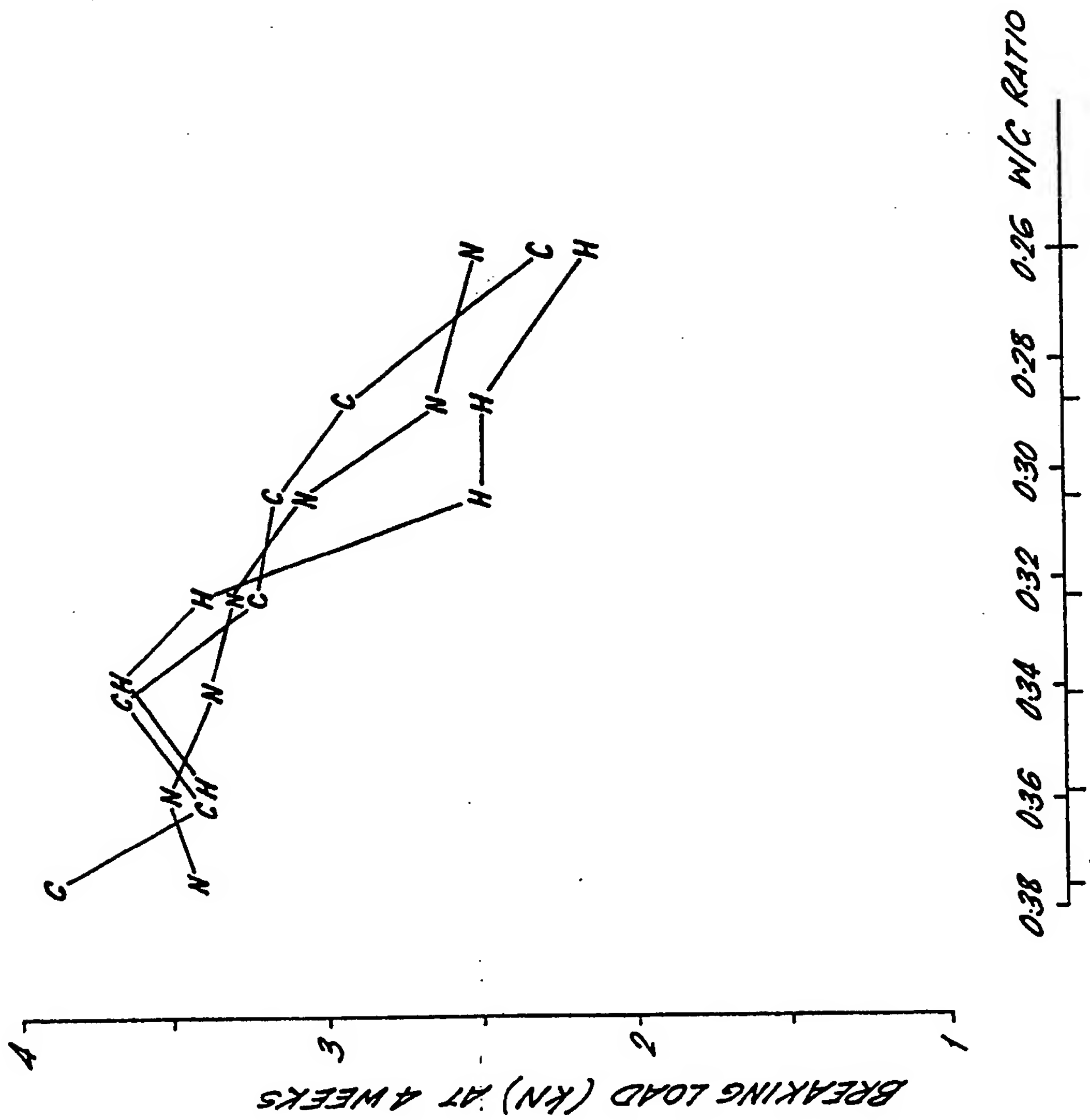
FIG.6. CURED MORTAR POROSITY vs W/C RATIO

7/9

FIG. 7. MERCURY INTRUSION PORE VOLUMES FOR CHAMBER-CURED TILES.

FIG. 8. MERCURY INTRUSION PORE VOLUMES FOR CARBONATED TILES.

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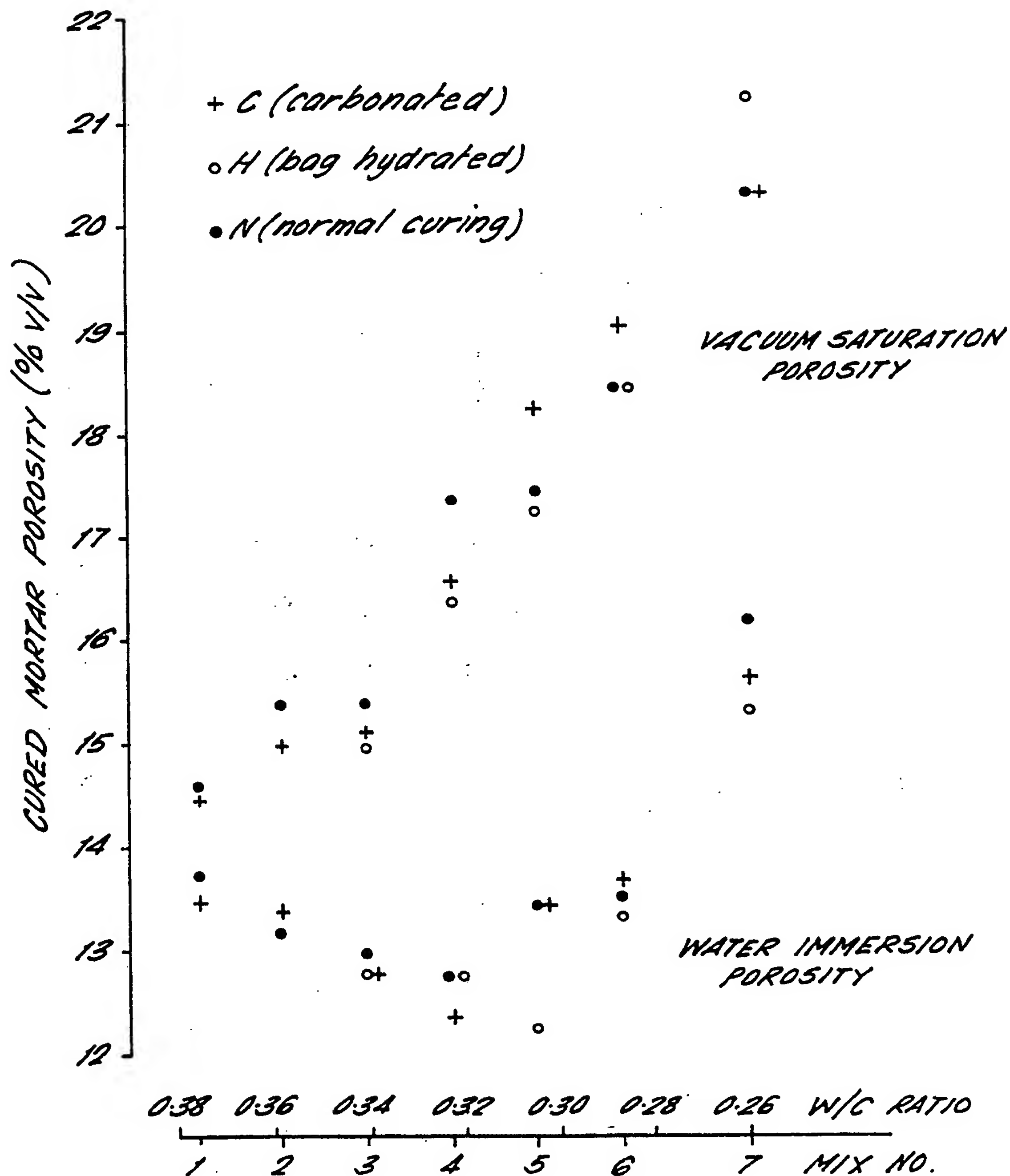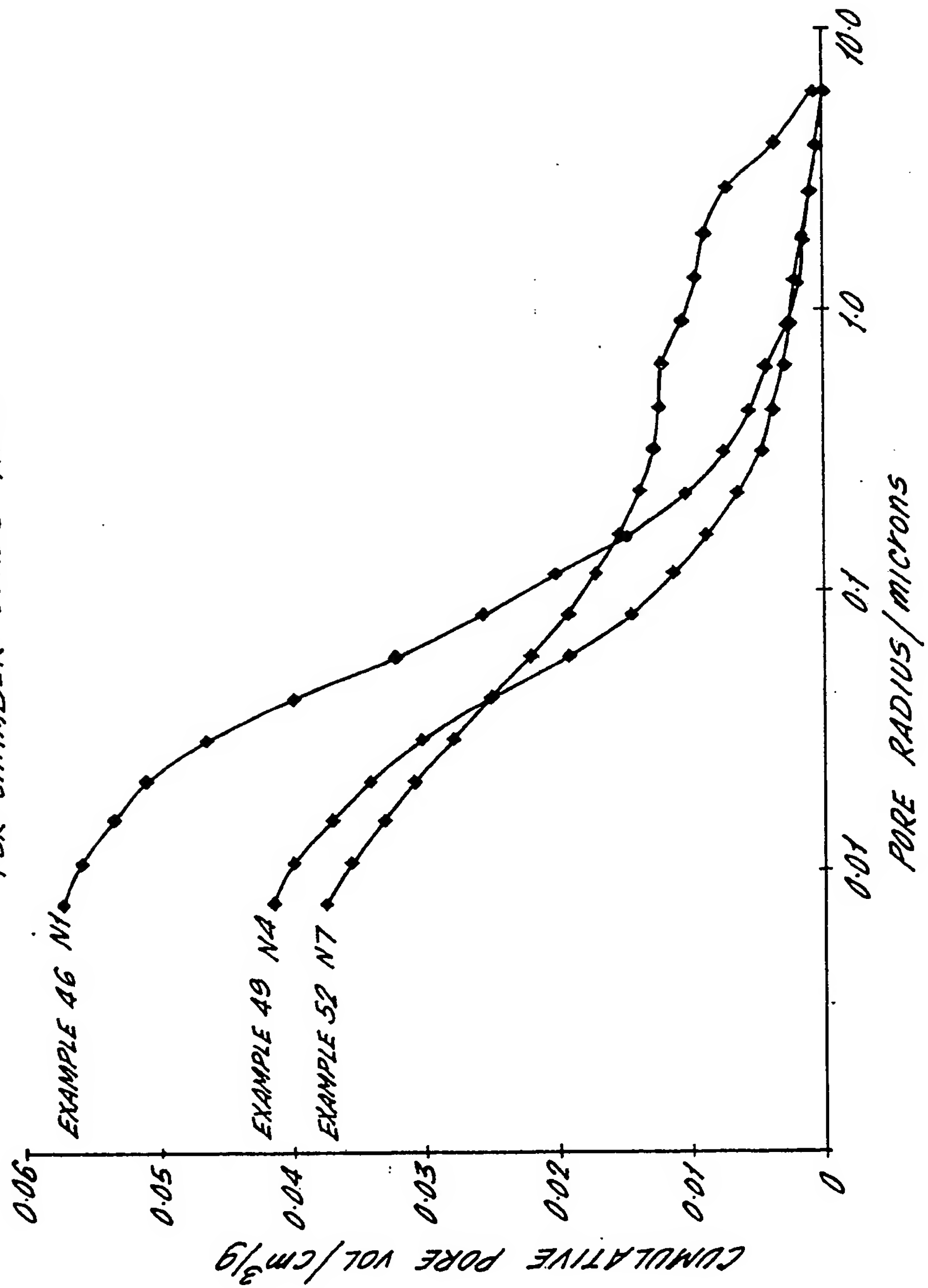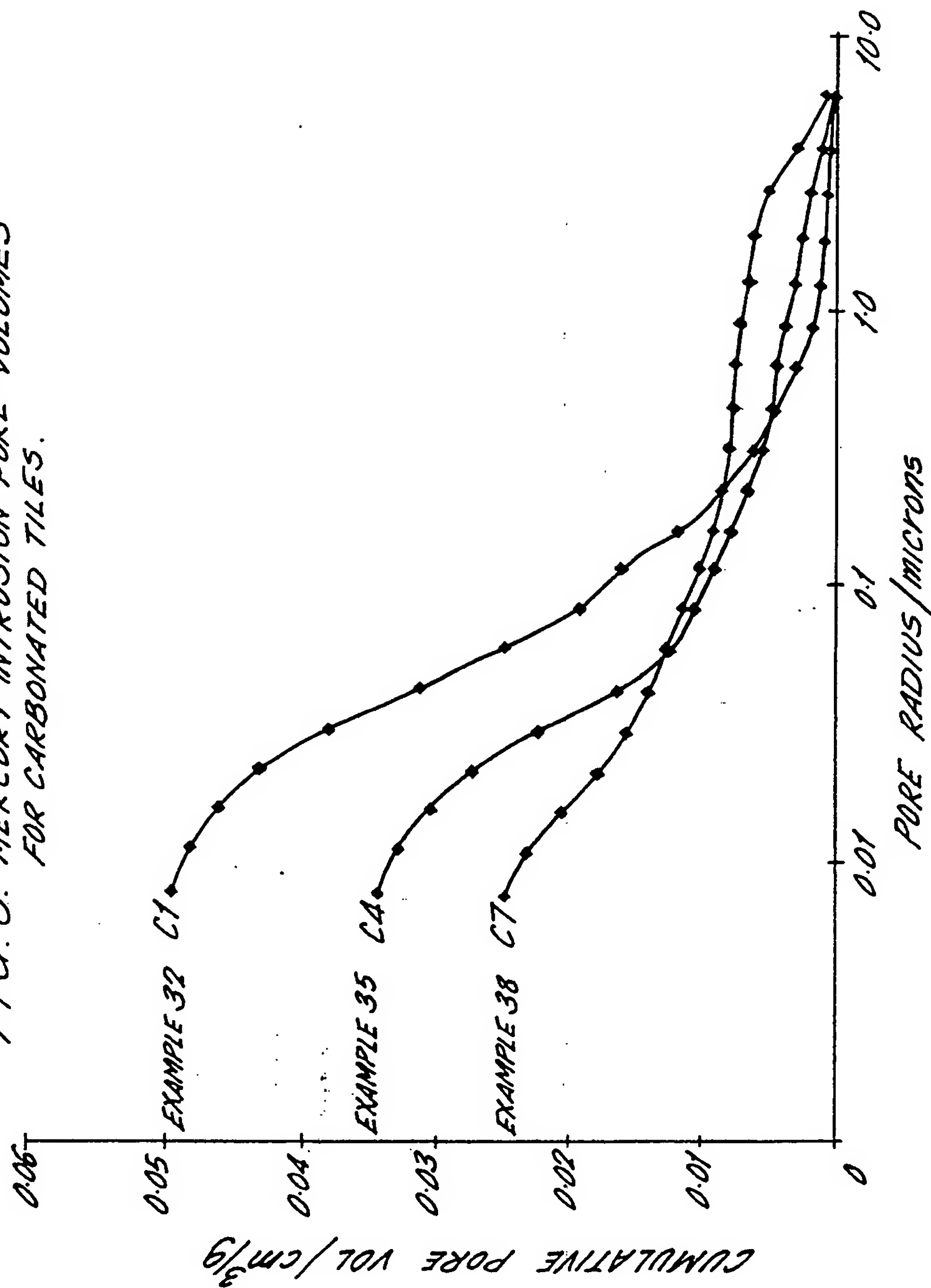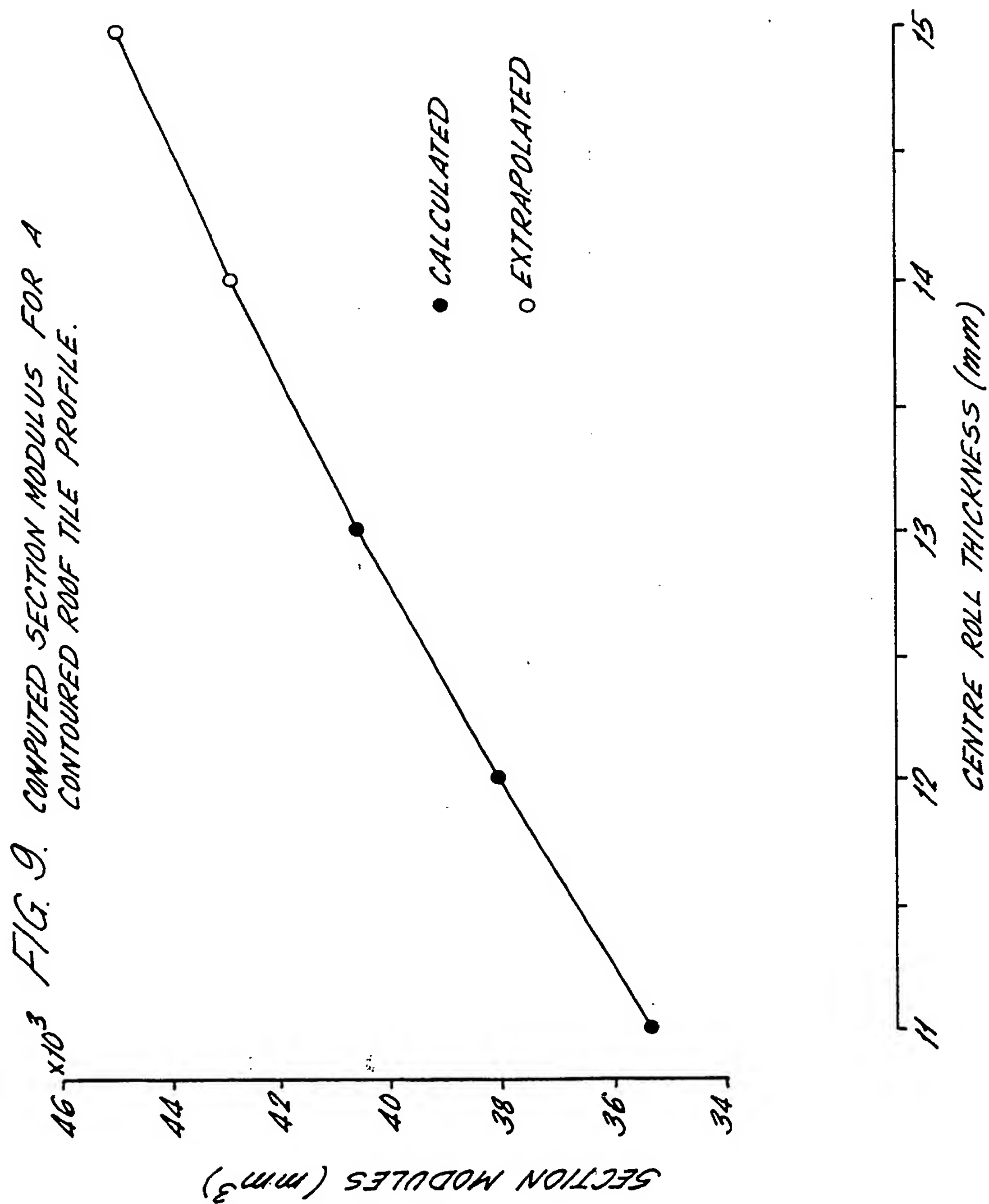FIG. 9. COMPUTED SECTION MODULUS FOR A CONTOURED ROOF TILE PROFILE.

SPECIFICATION

Improvement in concrete articles

5   This invention is concerned with improvements in concrete articles and is particularly concerned   5
with an improved method of manufacture of extruded concrete roof tiles, whereby their curing
time is much reduced by carbonation, and an improved tile making machine for effecting said
method.
    The process and apparatus for the manufacture of concrete roof tiles are both well known. A
10 relatively dry mortar mix of sand, cement and water usually in a ratio of about 3.5:1:0.4 is fed   10
usually via a hopper and a shaping roller to form a continuous strip of mortar on a succession of
pallets. The strip is subsequently cut at the junctions between the pallets to form individual
green tiles, the green tiles on the pallets are cured and then the tiles are split from the pallets.
    It will readily be appreciated that the requirement for pallets, in tile manufacturing methods
15 where tiles are produced at up to 150 tiles per minute, together with the extensive storage   15
space required for curing up to 100,000 tiles per shift, represents a very large investment. In
addition, when one considers the maintenance required to keep the pallets and curing chamber
in good working order, the initial outlay and ongoing costs for a tile producer are considerable.
Thus, there are obvious advantages to be gained by: a) reducing the time that is required before
20 a tile may be removed from its pallet without damaging the "green-state" product, and b)   20
obviating the need for extensive curing facilities.
    Many proposals have previously been made for speeding up the curing of mortar mixes but so
far none of these proposals has been capable of adoption in the manufacture of concrete roof
tiles.
25 The use of carbon dioxide in the curing of mortar is well known but no process hitherto   25
disclosed has been suitable for using in the manufacture of concrete roofing tiles where the
quality and durability of the end products is to be ensured.
    It is known to use carbon dioxide to harden concrete products, pre-cast tiles for example,
which are self supporting before carbonation and which are removed from the mould before
30 curing. Such processes are disclosed in, US 4093690, US 4117059 and US 4436498. US   30
4093690 and US 4117059 also disclose that the presence of 1–2% by weight of a vinyl
acetate – dibutymaleate copolymer is required before the carbonation reaction will procede.
    US 3468993 also discloses the carbonation of self-supporting concrete products; here the
products are carbonated after having been subjected to high pressure static compaction of at
35 least 500psi and removed from their moulds. US 4117060 discloses the simultaneous compac-   35
tion and carbonation of mortar within a mould.
    US 4427610 discloses the curing of mortar by exposing the concrete shape, following com-
paction, to ultra-cold carbon dioxide to provide those shapes with early strength.
    US 4069063 discloses the use of carbon dioxide added homogeneously to the cement slurry
40 during the water-cement mixing stage in order to control setting of the cement and to stabilise   40
the hydrated cement.
    GB 1337014 discloses a process for producing concrete blocks involving presetting the blocks
by injecting excess steam into the production zone and then by carbonating them.
    GB 2106886-A discloses a method for the rapid hardening of concrete and similar materials
45 by carbonation which involves the drying out of the capillary system of the concrete prior to and   45
during carbonation. The drying process is a necessary feature of this invention and may be
effected by a combination of air flow, heat generation and moisture absorption and, optionaly,
vacuum treatment. Also disclosed in this specification is a device designed for the carrying out
of the method of the invention.
50 None of the prior art specifications discloses a process suitable for carbonating extruded roof   50
tiles at atmospheric or only slightly supra- atmospheric pressured, nor do they disclose the
carbonation of non-preset concrete products without earlier pre-carbonation steps. A study of
the prior art moreover would suggest that additives such as the copolymers of US 4093690 and
US 4117059 are necessary in order to carbonate concrete products successfully.
55 Our studies made in the course of the development of the present invention have surprisingly   55
shown that products such as roof tiles can be readily carbonated by simple adaptations of the
processing conditions and apparatus used hitherto.
    We have now developed a method for the extrusion of concrete roof tiles which are not self
supporting before carbonation but which, after carbonation, can be readily removed from their
60 pallets without damage so that the pallets may be quickly reused.   60
    In order to remove the roof tiles from the pallets shortly after production it is necessary for
the tiles to be self supporting immediately after a fifteen minute curing process. This strength
makes it possible to remove the tiles easily and without damage from the pallets and the fifteen
minute time scale enables the pallets to be returned to the tile making machine quickly thus
65 greatly reducing the number of pallets required and removing the requirement for extensive   65

curing facilities for soft tiles.

The present invention relates to a method of manufacturing concrete roof tiles which are self supporting after fifteen minutes curing.

Accordingly, the present invention provides a method of manufacturing concrete roof tiles
5 wherein the void content (as hereinafter defined) of the fresh uncured mortar may conveniently   5
be from 14 to 23% preferably from 18 to 23%, and more preferably from 19 to 21%, and
where carbon dioxide or a carbon dioxide containing medium is used to accelerate the curing of
the mortar.

The ratios of sand to cement to water that are required to produce mortars of the desired
10 void content will vary with the different types of sand and cement that are suitable for the   10
preparations of the mortars for the method of this invention.

Many different sands and cements as hereafter defined can be used to prepare the mortar.

In general however a water/cement ratio of from 0.15 to 0.32, preferably from 0.26 to 0.30,
is required to produce fresh mortars having the desired void content.
15 The sand to cement ratio should generally lie in the range of from 2.5 to 4.5, preferably from   15
3.0 to 4.0.

While the high void content of the mortar and porosity of the tiles of the present invention is
an advantage in that it permits rapid diffusion of carbon dioxide through the mortar in the
carbonation stage it may also permit water to pass through the tile while it is in use. Water
20 passes most readily through the larger pores while carbon dioxide will diffuse through much   20
smaller pores; so in a preferred embodiment of the invention there is a restriction on the void
size, preferably this will not exceed, in the fresh mortar 0.5mm, more preferably it will not
exceed 0.2mm.

In order to ensure that carbon dioxide can permeate the mortar to carbonate it, the gas
25 permeability of the fresh mortar should preferably exceed 10^{12}m/s. If the permeability is less   25
than 2×10^{-13}m/s then the carbon dioxide will not be able to diffuse quickly through the mortar
and carbonation will be very slow. On the other hand if the permeability is too great, the
cohesion of the tile becomes reduced and the finished product is more open to water penetra-
tion.
30 Preferably the carbon dioxide is introduced to the fresh mortar at atmospheric pressure but it   30
may be introduced at an elevated pressure of up to 5 atmospheres. The percentage of carbon
dioxide in the carbonating atmosphere is preferably from 75% to 100%, more preferably 95% to
100%. In one preferred embodiment of the invention gaseous carbon dioxide is introduced to
the mortar in an air tight chamber, which has been previously evacuated, so that air is excluded.
35 As the carbonation reaction procedes more quickly at elevated temperatures, it is preferred to   35
preheat the mortar to a temperature of from 10 to 40°C, more preferably of from 20 to 30°C.
Fig. 1 shows the induction period (the difference in time from the introduction of carbon dioxide
to the mortar to the commencement of the carbonation reaction) plotted against initial mortar
temperature and shows clearly the effect of preheating the mortar. In one preferred arrangement
40 the heat of the carbonation reaction is recycled to preheat the mortar.   40
In one arrangement the carbon dioxide is introduced to the mortar when the mortar is
compacted on the pallets and preferably before the mortar is cut to provide individual tiles on
the pallets.

A convenient way of introducing the carbon dioxide to the mortar is via appropriate apertures
45 in the region of the slipper plate.   45
The pallets may be arranged to be permeable or may be provided with appropriate apertures
allowing the passage of fluid emanating from the carbon dioxide containing medium.

An alternative would be for the carbon dioxide to be introduced into the mortar prior to the
mortar being extruded. For exampe this could be done in the hopper.
50 It is to be understood that all the above references to carbon dioxide include the carbon   50
dioxide in liquid, gas or solid form and also include carbon dioxide containing mediums such as
carbonated liquids.

The invention also provides apparatus for making concrete roof tiles in which use is made of
any of the above method steps.
55 There now follows descriptions of an embodiment of a suitable plant lay out and of an   55
improved tile making machine according to the invention. These descriptions are to be read with
reference to the accompanying Figs. 2 and 3 respectively.

One embodiment of a suitable plant lay out for the apparatus of the present invention is
illustrated in Fig. 2. The sand, cement, water and additives such as pigment are mixed in the
60 batch mixer, the mortar is then transferred to the tile machine where the tiles are shaped on the   60
pallets, the tiles are then transferred via the indexer to the carbonation chamber to which carbon
dioxide has been introduced via the vaporiser. The heat generated in the carbonated reaction is
recycled by the heat exchanger to the batch mixer to preheat the mortar and to the vaporiser.
Following carbonation the tiles on their pallets procede via the indexer to the depalleter where
65 they are separated, the pallets returning to the tile machine while the tiles procede via the   65

collater and packer to the yard to mature.

An alternative embodiment of the invention is shown in Fig. 3; this is an illustration of the tile making machine where the carbon dioxide is introduced to the fresh mortar via an aperture in the slipper plate.

5   The machine 10, shown in the drawing, comprises a conveyor 11 of a conventional design, having drive dogs 12 by which pallets P are fed seriatim through a tile machine station 14.

At the station 14, the machine 10 is provided with a mortar hopper 15 and a mortar conveyor 16, by which, when the machine is in use, the hopper is charged with concrete mortar 17.

10   The hopper 15 is provided with tined compaction device 18, a conventional compaction roller 19 and a slipper 20, which roller and slipper define, together with pallets P passing beneath the hopper 15 when the machine is in use, a slit-like opening, through which mortar will pass to form a ribbon of mortar 22 on said pallets P.

For supporting the pallets P, as they pass beneath the hopper as aforesaid, the machine 10 is
15   provided with a dead-bed 23 also of conventional design. .

The slipper 20 of the machine 10 is provided with an inlet 24 extending downwardly there-through, which inlet 24 is connected to a cylinder 25, fixedly mounted on the slipper 20.

When the machine 10 is in use and tiles pallets P are conveyed beneath the hopper 15 as aforesaid, by pressurising the cylinder 25, CO_2 in gaseous and/or liquid form is caused to pass
20   thorugh said inlet 24 and into the mortar 17 via a porous plug (not shown) as it passes underneath the slipper. The CO_2 is diffused throughout the mortar ribbon 21 to cause accelerated hydration thereof.

Immediately after exiting from the slipper, the ribbon of mortar 21 is cut by a knife, or knives, not shown, to form discrete green-state tiles on the pallets P
25   ''Green-state'' tiles formed as aforesaid and made from a mortar comprised of a 3.5:1.0:0.3 sand, OPC, water mixture were found to have a flexural strength of 1.9 MPa after 15 minutes. This early strength enables the separation of the ''green-state'' tiles from their respective pallets thereby releasing the pallets for subsequent tile making operations.

Traditionally, tile pallets for the production of concrete roof tiles are made of metal and are
30   somewhat impervious by nature. It is envisaged that, in the present invention, pallets made from a porous material will enhance the diffusion of the CO_2 gas through the tile mortar.

It is also foreseen that more than one inlet for CO_2 may be provided on the slipper along the length thereof and that inlets may also be provided in the check plates usually extending along the sides of the tile mortar adjacent to said slipper.

35   Obviously, the amount of CO_2 utilised will depend upon the mass and nature of mortar being used to form the tiles and it is considered that the gas and/or liquid CO_2 may be fed to the various inlets at the same, or differential pressures, as required. Such a facility will be important where the cross section of the tiles being formed is not constant.

If required, the ''green-state'' tiles may be subjected to further CO_2 treatment before, or after,
40   separation from their pallets P by passing them through a treatment chamber downstream of the tile making station 14.

The invention is further illustrated with reference to the following Examples in which the sands and cements utilised have the sieve analyses and characteristics as shown in Tables A and B hereinafter.

45   The sands are basically quartz sands, i.e. they are high in silica content.

TABLE A

SAND CHARACTERISTICS

SIEVE SIZES (Cumulative % Passing By Weight)

DESIGNATION	(mm)	4.75	3.35	2.36	1.18	0.6	0.3	0.15	Silt
A		100		98.9	91.5	65.7	16.0	1.6	5.5
B		98.9		80.3	65.2	52.5	26.5	2.1	7.8
C		99.2	93.7	87.2	75.8	57.9	18.7	2.8	4.7
D		99.7	95.9	86.1	70.3	51.3	20.5	4.2	7.2
E		100		99.2	93.6	64.8	14.4	2.2	14.7

TABLE B

CEMENT CHARACTERISTICS

Designation	F	G	H	I	J	K
CHARACTERISTS						
Specific surface area (m²/kg)	346	378	362	303	466	486
Oxide analysis (%)						
— SiO₂	21.0	19.8	19.4	19.3	19.6	20.1
— Al₂O₃	4.2	5.4	5.2	5.2	5.1	5.0
— Fe₂O₃	1.9	2.5	3.0	3.0	2.9	2.4
— CaO	65.3	64.0	65.2	64.7	64.8	65.6
— MgO	1.0	1.3	1.3	1.2	1.2	0.9
— SO₃	2.5	2.9	2.8	3.3	3.2	2.4
— K₂O	0.61	0.8	0.65	0.75	0.68	0.71
— Na₂O	0.14	0.2	0.17	0.17	0.15	0.10
— Loss on ignition	1.9	2.4	1.5	1.6	1.6	1.4
— free lime	2.1	1.2	0.6	0.6	0.7	1.1
Lime saturation factor	97.7	97.5	101.2	100.3	99.5	100.1
Bogue compound composition(%)						
— C3S	59.6	61.9	68.3	65.6	64.5	66.0
— C2S	15.2	10.1	4.1	5.8	7.6	7.9
— C3A	7.9	10.1	8.7	8.7	8.6	9.2
— C4AF	5.8	7.6	9.1	9.1	8.8	7.3
Initial set (mins)	195		130	150	85	80
Final set (mins)	265		205	215	145	140
Standard consistency (%)	26.3		26.3	25.5	26.5	25.5

The data in Table B above were obtained by the methods outlined in British Standards No. 12:1978 (Ordinary and rapid-hardening Portland Cement) and No. 4550:1978 (Methods of Testing Cement) with the exception of the Bogue compound compositions which were calculated according to the formulae given in A.S.T.M. Standard C 150-85 (Portland Cement)

EXAMPLES 1–29

Tiles were prepared from cements, sands and water in the proportions set out in Table 1 with the optional addition of red oxide pigment (Deanshanger 'L12'), plasticiser (Sika 'Plastiment – BV40') or air-entrainer (Cementation Chemicals "Cemairin').

5   Sand and cement were mixed dry in an Eirich Pan mixer together with any additives for 1 minute, the sand/cement ratio being a constant 3.5. Water was then added in the water/cement ratios listed in column 2 of Table 1, and the mixture was mixed for a further 3 minutes.

The tile machine was an ordinary commercial tile making machine used under laboratory conditions although it was used in its standard settings, i.e., the ones normally used for tile

10   commercial production. The tile machine hopper was filled with mortar which was compacted under the slipper by running the roller on its own for a few seconds to ensure that the first few tiles of each run (corresponding to one mortar batch) were of reasonable quality. Four tiles were selected from each run and two were subjected to accelerated carbonation, while the other two were bag cured for 24 hours.

15   The accelerated carbonation procedure involved the placing of the two tiles on their pallets in a plastic bag (55×88cm) which was inflated by injecting CO_2 (from a liquid cylinder via a vaporiser at rates up to 30 litre/minute) to maintain a slight positive pressure for fifteen minutes. The mortar temperature was monitored throughout the fifteen minutes by means of a thermo-couple probe.

20   Various properties of the fresh mortar and of the carbonated tiles were investigated. Of the newly carbonated tiles, the strength (columns 7 and 9 of Table 1), the surface appearance (column 10) the Ridsdale weight (column 11), of the fresh mortar the percentage of the voids (column 12), and of the cured mortar porosity (column 13), were measured.

Measurements of these properties were carried out as described below.

25

Strength Testing

The strengths of both carbonated specimens of each example were determined as soon as possible after carbonation by means of 3-poing transverse loading. For breaking loads below 200N, tiles were tested using the Salter Force Gauge mounted on a drill stand, adapted to load

30   transversely on bearer rods 350mm apart with a central load bar resting on the two rolls of the tile.

When breaking loads exceeded 200N, tiles were tested at a span of 280mm on a B.S. tile breaker. Such tile breakers give breaking loads which are about 15% higher than those given by an Instron "1116" Universal Testing Machine.

35   Transverse breaking loads have been converted into apparent mortar bend strengths by means of the formula

$$P = \frac{W.S}{4z}$$

40

where P is the strength in MPa
   W is the breaking load in N
   S is the bearer span in mm

45   and z is the section modulus in mm³.

Values of z, computed for a contoured tile with a range of centre roll thicknesses, are plotted in Fig. 9. The 'apparent' strength thus calculated assumes that the load is applied 'ideally' (i.e. distributed to avoid stress concentation), but it has been found in practice that 'real' strengths measured in the tile mortar may be up to 50% higher than 'apparent' strengths obtained from

50   tile-breaker loads.

Apparent strengths were calculated from the mean of two breaking loads. Because of the difficulty in ensuring complete removal of air from the bag prior to carbonation, one tile always appeared to be less well carbonated and therefore weaker than the other, so that quoted mean strength is probably an underestimate of what could be achieved with a better engineered

55   carbonating system.

Surface Appearance

Surface appearance was rated by Comparison with non-carbonated tiles on the following scale:
   5—excellent

60   4—good
   3—acceptable
   2—poor
   1—very poor.

Ridsdale Weight

65   The Ridsdale weight is defined as the weight of a block of mortar of 188cm³ which has been   65

rammed to that constant volume.

Percentage of Voids in Fresh Mortar

The Fresh Mortar Void content is defined as

5   $E(\%) = 100(1 - D/D_o)$ 5

where D is the mortar density as measured on a cylinder of mortar rammed to constant volume
on a Ridsdale sand Rammer and Do is the theoretical void free mortar density defined as

$DO = A + 1 + W/\{A/P_a + 1/P_c + W\}$

10 for an aggregate: cement: water ratio of A:1:W and for aggregate and cement densities of P_a 10
and P_c respectively.

Cured Mortar Porosity

The cured mortar porosity is measured by the normal water saturation method.

15   Examples 1–6 illustrate the effect of reducing the water/cement ratio while keeping other   15
variables constant for a Sand "D"/.cement "F" mixture. Examples 7–10 illustrate the same
effect when Cemairin air-entrainer is added to the mixture, examples 11–16 when BV40 plasti-
ciser is added and Examples 17–20 when pigment 5 red oxide pigment is added. Examples
22–25 illustrate the effects of using different sands at a constant sand/cement ratio of 0.30,
20 and examples 26–29 show the effects of using different cements.   20
Maximum apparent strength after 15 minutes is achieved at low or intermediate water/cement
ratios. The apparent strength is plotted against w/c ratio in Fig. 4.
The carbonation process is tolerant of a wide range of sands, but Sands "D", "A" and "C"
give the highest 15 minute strengths; in general the mortars with the highest void content
25 produce the highest 15 minute strengths. Similarly the process is tolerant of a range of cements   25
with cements "G" and "F" giving the highest 15 minutes strengths.
The addition of pigment, plasticiser or air-entrainer tends to slightly reduce both mortar void
content and fifteen minute strength but not by any significant amount. That the addition of air-
entrainer should decrease void content may indicate that its plasticising characteristics predomi-
30 nate at the comparatively high ramming pressures used.   30
The monitoring of mortar temperature during the carbonation showed that it would be possible
to increase the temperature of mortar, pallets and other apparatus to a temperature of at least
20°C at which the carbonation reaction may procede more quickly.

35 *EXAMPLE 30*   35
The procedure of the earlier examples was repeated except that the aggregate/cement/water
ratio was 4.5/1/0.3. The results are tabulated in Table I, cement "F" and sand "D" were used,
no additives were added. The effect on 15 minute strength was not great, nor was the effect
on porosity, of changing the aggregate/cement ratio.
40   40
EXAMPLES 31–51
In these examples the investigations undertaken for the tiles of examples 1–30 were continued
and extended under actual works conditions rather than under laboratory conditions. Compari-
sons between carbonated tiles (examples 31–37), bag hydrated tiles (examples 38–44) and
45 chamber cured tiles (examples 45–51) were carried out.   45
The tiles were prepared from the cements, sands, water and admixture in the proportions set
out in Table 2. Sand "E" and cement "K" were used, the pigment was a commercially available
iron oxide pigment. The tiles were prepared using an ordinary commercial tile machine in its
standard settings.
50   Following manufacture of the tiles, of the tiles from each mix, 4 were carbonated, 2 were bag   50
cured and 8 were chamber cured. When more than one tile was tested to ascertain a particular
property an averaged result is quoted.
The carbonated tiles were carbonated by the process described in examples 1–30 and are
designated C. The bag cured tiles, designated H, were sealed on their pallets in polythene bags
55 and left to hydrate at ambient temperature (between 5 and 15°C) for 48 hours. The chamber   55
cured tiles were subjected to the normal chamber curing cycle, and are designated N.
The strength of the depalletable carbonated tiles was measured after 15 minutes carbonation.
The tiles of Examples 31–37 are prepared for mixes 1–7 of Table 2. Their strength was
measured using three-point flexure on parallel bearer rods 350 mm apart, with a central bar
60 resting on the two rolls of the tile loaded by means of a Salter Force Gauge mounted on a drill   60
stand.
Example 31 prepared from the mortar from Mix 1 showed no change after carbonation, and
tiles were therefore not depalletable. Example 32, tiles from Mix 2, had developed a slight
surface crust, especially on the locks where the mortar is less well compacted, but were still not
65 depalletable. The surface crust was more evident in Example 33 prepared from Mix 3, but only   65

with Example 34 (Mix 4) had sufficient strength been developed for tiles to be depalleted: unfortunately they were not quite strong enough to support their own weight and could there- fore not be tested for strength. Tiles from the remaining mixes (examples 35–39) were all easily depalletable and yielded strengths which increased with reduction in w/c ratio, and in some
5 cases exceeded the capacity of the Force Gauge (200N).
    The 15 minute strengths thus measured are listed in the final column of Table 2. None of the bag or chamber cured tiles could be depallated after this short curing time.
    The fact that the strengths of the carbonated tiles were lower than the strengths measured in examples 1–29 for similar w/c ratios is due to the fact that the carbonation reaction can
10 procede to a lesser extent in the tiles of the present examples which have been more highly compressed by the works-tuned tile manufacturing machine.
    The properties of the cured and matured tile samples were measured and the results obtained as described below.

15 *Flexural strength*
    After storing dry for 4 weeks, breaking loads were measured on dry tiles in 3-point flexure, using parallel bar breakers mounted at a span of 280mm in a model 1116 Instron running at a cross-head speed of 0.5mm/minute.
    The measured breaking loads are shown in Table 3: where more than one tile of a type was
20 tested, a standard deviation is given, together with the number of tiles tested in brackets. These results are plotted against w/c ratio in Fig. 5. There is little difference in strength between the three curing regimes at any of the mix w/c ratios, but reducing the w/c ratio from 0.38 to 0.26 causes the flexural strength to fall by more than 30%.

25 *Density and porosity of water immersion*
    Densities were measured, in triplicate, on samples about 5cm square cut from the valleys of the tiles. Two methods were used: the normal water immersion method and the more recently developed technique of vacuum saturation, where the specimens are placed in water under vacuum for 24 hours instead of merely being soaked in an open tank for 24 hours.
30 'Wet' (saturated and surface dry) and oven dry densities, determined densities, determined by water immersion, are tabulated for each mix in Table 4, which shows that there is a little difference between chamber cured (N), bag hydrated (H) and carbonated (C) densities at each w/c ratio. There is little fall in density with reduction in w/c ratio until the last two mixes.
    Porosities determined by the two techniques are tabulated in Table 5 and plotted as a function
35 of w/c ratio in Fig. 6. The values (numerically equal to the difference between wet and dry densities, expressed as a percentage) represent the void space which is accessible to water, and are less sensitive to the curing regime than to the original water content of the mortar mix. Whereas the 'vaccum saturated porosity' increased steadily with falling w/c ratio, the water immersed porosity reached a minimum at a w/c ratio of about 0.32. Since vacuum saturation
40 enables smaller pores to be filled by water, this suggests that the initial effect of w/c reduction (0.38 to 0.32) is to increase the number of small pores, and that the number of larger pores does not begin to increase until the w/c ratio falls below 0.32.

    Porosity by mercury intrusion
45 Selected specimens from Mix Nos. 1, 4 and 7; either carbonated or chamber cured (i.e. examples 31, 34, 37, 45, 48 and 51) were examined by mercury intrusion porosimetry (MIP), which measured pore volumes in the size range 0.005 to 7.5μm.
    The results of determinations in duplicate are presented in Figs. 7 and 8, where the cumulative pore volume (in cm^3/g) is plotted against the pore radius. These distributions show that the
50 porosity in this size range, and expecially below 1μm, actually falls with decreasing w/c ratio, in contrast to the results from water immersion testing. This is consistent with the known effect of w/c ratio on the capillary space within hardened cement paste.
    Carbonated tiles had a slightly lower porosity than chamber cured, presumably because deposi- tion of calcium carbonate during carbonation blocks the finer pores.
55

    Mortar microstructure
    6 tile samples of the same tiles that were used for measuring mercury intrusion i.e. Examples 31, 34, 37, 45, 48 and 51 have been examined by back-scattered electron imaging (BSEI). This technique produces an image on the electron microscope whose contrast varies with the atomic
60 number density of the phases present, and can thus distinguish easily between pores, cement paste and aggregates in mortar. In addition, it is possible to feed the electron image into a versatile multi-colour image analyser which enhances the contrast and can quantify the propor- tions of phases present and perform statistical operations on them.
    Before polishing to a flat surface with 1μm diamond paste, specimens were impregnated with
65 polymer to enhance the contrast of the pores. It was estimated that the magnification used

(×100), the image analysing system was capable of resolution down to about 50μm.

The relative volumes of phases present in mortars, obtained from averaging 4 or more fields for each specimen, are shown in Table 6.

As expected, porosity increased with reduction in w/c ratio from mixes 1 to 4 to 7, and there was little difference between carbonated and chamber cured specimens or between roll and valley sections. The porosity of examples 31 and 45 was considerably less than that measured by water immersion, probably because the more viscous resin was less able to penetrate the smaller pores.

Pore size distribution

Electron microscopy of tile sections (see above) has suggested that lowering the w/c ratio of tile mortar may affect both the spatial and size distribution of porosity. Volume porosities determined by different techniques are compared in Table 7. The pore size range covered by mercury instrusion (MIP) is related to the pressure used and the contact angle of mercury: the ranges for water immersion and vacuum saturation have been estimated assuming that water will penetrate all the capillary (but not gel) pores in the cement paste under vacuum, but will not reach the smaller capillary pores if no vacuum is applied.

The data in Table 7 shows that with decreasing w/c ratio

(i) porosity below 1μm (MIP) falls

(ii) porosity between 1 and 7.5μm (MIP) rises

(iii) the 'total' porosity (water under vacuum) rises

(iv) the smaller water-accessible porosity (difference between vacuum saturation and immersion) rises.

This last observation conflicts with the first, suggesting that the type or shape of pores penetrated by mercury and water may be different. Nevertheless, comparison of the mercury and water pore volumes indicates that the large porosity (greater than a few μm) increases considerably with decreasing w/c ratio.

TABLE 1   Summary of Run Parameters

Examples	w/c Ratio	Cement (if not Cement "F")	Sand (if not Sand "D")	Additive (Dosage w/w cement) (%)	Tile Wt. (g)	Mean Load (N)	Thickness	Apparent 15 minute (MPa)	Surface Appearance (1–5)	Ridsdale weight (g)	Estimated voids(%) in Fresh mortar	Cured porosity (%)
1	0.36				–	–	–	–	3	374	18.1	17.1
2	0.34				4959	101	13.366	0.21	3	382	16.8	16.8
3	0.32				4960	108	14.017	0.22	3	380	17.8	16.8
4	0.30				4904	460	14.000	0.75	3	370	20.4	16.7
5	0.28				4650	555	13.670	0.92	3	365	22.0	16.9
6	0.26				4667	557	13.627	0.93	2	365	22.5	17.0
7	0.34			Cemelrin 0.12	4717	145	13.53	0.30	3	385	16.2	–
8	0.32			Cemelrin 0.12	4625	124	14.01	0.25	3	–	–	–
9	0.30			Cemelrin 0.12	–	166	14.10	0.32	3	385	17.2	–
10	0.28			Cemelrin 0.12	4628	320	13.83	0.53	3	–	–	18.8
11	0.34			BV40 0.5	4973	752	13.67	0.16	4	381	17.0	18.8
12	0.32			BV40 0.5	5070	87	13.97	0.18	5	379	18.0	19.5
13	0.30			BV40 0.5	4958	201	14.35	0.33	3	379	18.5	19.9
14	0.28			BV40 0.5	4934	340	13.994	0.55	3	375	19.8	–
15	0.26			BV40 0.5	4475	260	13.78	0.43	2	369	21.6	–
16	0.24			BV40 0.5	4610	380	13.50	0.64	4	366	22.7	–
17	0.34			Pigment 5	4792	215	13.4	0.36	3	–	–	20.1
18	0.32			Pigment 5	4797	210	13.51	0.35	1	381	17.6	20.7
19	0.30			Pigment 5	4840	380	13.40	0.64	4	369	20.6	–
20	0.28			Pigment 5	4701	310	13.31	0.53	2	365	22.0	–
21	0.26			Pigment 5	4451	280	12.96	0.48	2	–	–	21.8
22	0.30	"A"			4709	325	13.30	0.55	4	390	16.1	21.6
23	0.30	"E"			4829	105	12.88	0.23	5	398	14.4	–
24	0.30	"C"			4851	179	12.86	0.39	4	387	16.8	–
25	0.30	"B"			4790	64	13.41	0.13	2	387	16.8	–
26	0.30		"G"		4788	395	13.44	0.66	3	373	19.8	–
27	0.30		"H"		4677	208	12.97	0.36	2	–	–	–
28	0.30		"I"		4582	210	13.26	0.34	3	–	–	–
29	0.30		"J"		4664	210	13.00	0.36	2	–	–	–
30	0.30		"D"		4650	305	13.70	0.51	2	362	22.1	20.5

at 4.5 s/c

TABLE 2   CONTOURED TILE MAKING MACHINE

	Measured batch weights					Estimated		Calculated mix parameters			Machine parameters			Breaking loads after 15 min. carbonation	Ex.
Mix No.	Wet Sand (kg)	Cement (kg)	Pigment Solid (kg)	Pigment Water (l)	Water added (l)	Total water (l)	Water in sand (l)	Dry a/c ratio	W/C ratio	Moisture content (%)	Mean tile thickness (mm)	Tile weight (g)	'Density factor'		
1	752	223	10.2	11.9	48	84	24	3.26	0.376	8.0	(10.70)	4736	443	-	31
2	752	223	10.2	11.9	43	80	25	3.26	0.359	7.7	10.71	4545	424	-	32
3	752	223	10.2	11.9	38	76	26	3.26	0.341	7.3	10.78	4509	418	-	33
4	752	223	10.2	11.9	33	72	27	3.25	0.323	7.0	10.75	4520	421	(50)	34
5	752	223	10.2	11.9	29	68	27	3.25	0.305	6.6	10.76	4454	414	54.79	35
6	752	223	10.2	11.9	25	64	27	3.25	0.287	6.3	10.85	4418	407	159 200	36
7	752	223	10.2	11.9	19	58	27	3.25	0.260	5.7	10.83	4280	395	200 200	37

TABLE 3   Breaking loads for tiles tested at an
             age of 4 weeks

CURING REGIME

MIX	(EXAMPLES 45-51) N	(EXAMPLES 38-44) H	(EXAMPLES 31-37) C
1	3410+190(4)	–	3900
2	3460+260(4)	3400	3400
3	3350+280(4)	3650	3630+40(2)
4	3260+540(4)	3380+250(2)	3200
5	3060+280(4)	2450	3100
6	2590+190(4)	2450	2910+420(4)
7	2440+100(4)	2100	2260+430(5)

TABLE 4   'Wet' (saturated and surface dry) and oven dry
          densities determined by water immersion
          (means of 3 samples).

Example No.	Wet density			Dry density		
	(45-51) N	(38-44) H	(31-37) C	(45-51) N	(38-44) H	(31-37) C
Mix No.						
1	2.336	–	2.319	2.198	–	2.184
2	2.340	–	2.368	2.207	–	2.233
3	2.340	2.330	2.339	2.210	2.202	2.210
4	2.345	2.347	2.300	2.216	2.219	2.176
5	2.321	2.329	2.341	2.186	2.206	2.206
6	2.315	2.332	2.309	2.179	2.198	2.172
7	2.294	2.248	2.294	2.131	2.094	2.137

TABLE 5   Porosities determined by water immersion and by
             vacuum saturation

Example No. Mix No.	Water immersion porosity (%)			Vacuum saturation porosity (%)		
	(45-51) N	(38-44) H	(31-37) C	(45-51) N	(38-44) H	(31-37) C
1	13.7	-	13.5	14.6	-	14.5
2	13.2	-	13.4	15.4	-	15.0
3	13.0	12.8	12.8	15.4	15.0	15.1
4	12.8	12.8	12.4	17.4	16.4	16.6
5	13.5	12.3	13.5	17.5	17.3	18.3
6	13.6	13.4	13.7	18.5	18.5	19.1
7	16.3	15.4	15.7	20.4	21.3	20.4

TABLE 6   Relative volumes of phases in tile mortars,
             determined by back-scattered electron imaging.

Example No.	31 Roll	31 Valley	34 Roll	34 Valley	37	45	48	51
Volume %								
Pores	6	6	15	13	15	8	13	16
Sand	70	72	63	66	66	75	66	63
Hydrates	21	18	17	17	15	14	16	16
Clinker	3	4	5	4	4	4	5	5

TABLE 7 Porosities (volume %) determined by mercury intrusion, water immersion and vacuum saturation

Technique		Mercury porosimetry		Water immersion	Vacuum saturation
Size range	Max. Min.	1μm 5nm	7.5μm 1 μm	mm μm	mm nm
Example No.					
45		12.2	0.6	13.9	16.0
48		9.2	0.6	13.0	17.3
51		5.1	2.6	16.7	21.0
31		10.9	0.3	13.0	16.9
34		6.7	0.9	15.2	18.6
37		4.1	1.6	15.0	21.3

CLAIMS

1.   A method of manufacturing concrete articles wherein the void content (as hereinbefore defined) of the fresh mortar is from 14 to 23% by volume and wherein carbon dioxide or a carbon dioxide containing medium is used to accelerate the curing of the mortar.

2.   A method as claimed in Claim 1 wherein the void content of the fresh mortar is from 18 to 23% by volume.

3.   A method as claimed in claim 2 wherein the void content of the fresh mortar is from 19 to 21% by volume.

4.   A method as claimed in any one of the preceding claims wherein the water to cement ratio of the fresh mortar is in the range of from 0.15 to 0.32.

5.   A method as claimed in Claim 4 wherein the water to cement ratio is in the range of from 0.26 to 0.30.

6.   A method as claimed in any one of the preceding claims wherein the sand to cement ratio of the fresh mortar is in the range of from 2.5 to 4.5.

7.   A method as claimed in Claim 6 wherein the sand to cement ratio is in the range of from 3.0 to 4.0.

8.   A method as claimed in any one of the preceding claims wherein the largest pore size in the fresh mortar is 0.5mm.

9.   A method as claimed in Claim 8 wherein the largest pore size in the fresh mortar is 0.2mm.

10.   A method as claimed in any one of the preceding claims wherein the gas permeability of the fresh mortar is at least 2×10^{-13}m/s.

11.   A method as claimed in Claim 10 wherein the gas permeability of the fresh mortar is at least 10^{-12}m/s.

12.   A method as claimed in any one of the preceding claims wherein the carbon dioxide or carbon dioxide containing medium is used to accelerate curing at a pressure in the range of from 1 to 5 atmospheres.

13.   A method as claimed in Claim 12 wherein the pressure is 1 atmosphere.

14.   A method as claimed in any one of the preceding claims wherein the percentage of carbon dioxide in the carbonating atmosphere is from 75% to 100%.

15.   A method as claimed in Claim 14 wherein the percentage of carbon dioxide in the carbonating atmosphere is from 95% to 100%.

16.   A method as claimed in any one of the preceding claims wherein the mortar is preheated to a temperature of from 10 to 40°C before carbonation.

17. A method as claimed in Claim 16 wherein the mortar is preheated to a temperature of from 20 to 30°C before carbonation.

18. A method as claimed in Claims 16 or 17 wherein the heat of the carbonation reaction is used to preheat the mortar.

5   19. A method as claimed in any one of the preceding claims wherein the carbon dioxide or   5
carbon dioxide containing medium is introduced to the mortar on the pallets, preferably before it is cut to provided individual tiles.

20. A method as claimed in Claim 19 in which carbon dioxide is introduced to the mortar via appropriate apertures in the slipper plate.

10   21. A method as claimed in any one of Claims 1 to 19 wherein the pallets are permeable or   10
are provided with appropriate apertures for the flow of fluid emanating from the carbon dioxide containing medium.

22. A method as claimed in any one of claims 1 to 18 wherein the carbon dioxide is introduced into the mortar prior to the mortar being compated (e.g. on the hopper).

15   23. A method of manufacturing concrete roof tiles as claimed in any one of the preceding   15
claims and substantially as hereinbefore described with reference to the examples.

24. Apparatus for carrying out the method as claimed in any one of claims 1 to 23 or substantially as hereinbefore described with reference to the drawings.

25. A concrete roof tile produced by a method as claimed in any of claims 1 to 23.

20   26. A roof comprising a plurality of tiles as claimed in claim 25.   20

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